(19) THE PATENT OFFICE
2nd M. S. O. BUILDING
234/4, ACHARYA JAGADISH CHANDRA BOSE ROAD
CALCUTTA—700 020.

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(71) Applicant : M/S Rallis India Limited an Indian Company having its registered office at Rolli House, 21 D S Marg, Bombay 400001, Maharashtra, India

(72) Inventor :
1) MAKARAND MAHADEO PATANKAR
2) SHEKHAR VISHWANATH KHADILKAR
3) DR. RAJEEV SADASHIV DESHPANDE
4) DR. BIRJA SHANKER

(74) Agent : M/S. DePenning & DePenning Bombay

Examiner : Shri R. Bhattacharya

(54) Title : A PROCESS FOR THE PREPARATION OF THE INSECTICIDAL ENANTIOMERIC MIXTURE OF (S)-α-CYANO-3-PHENOXYBENZYL-(Z)-(1R)-CIS-3-(2-CHLORO-3,3,3-TRIFLUOROPROPENYL)-2,2-DIMETHYL CYCLOPROPANE CARBOXYLATE AND (R)-α-CYANO-3-PHENOXYBENZYL-(Z)-(1S)-CIS-3-(2-CHLORO-3,3,3-TRIFLUOROPROPENYL-2,2-DIMETHYL CYCLOPROPANE CARBOXYLATE, COMMONLY KNOWN AS LAMBDA CYHALOTHRIN.

(57) Abstract

A process for the preparation of the insecticidal enantiomeric mixture of (S)-α-cyano-3-phenoxy benzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2- dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxy-benzyl-(Z)-(1S)-cis-3(2-chloro-3,3,3-trifluoro propenyl0-2, 2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin by epimerisation crystallisation of cyhalothrin in an alcohol in the presence of 1,4-diazabicyclo (2,2,2) octane (DABCO) with pure crystals of the enantiomeric mixture as seeding agent at 20° to 0°C.

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178538

THE PATENTS ACT, 1970

COMPLETE

Specification

SECTION 10

The following Specification particularly describes and ascertains the nature of this invention and the manner in which it is to be performed :—

This invention relates to a process for the preparation of the insecticidal enantiomeric mixture of (S)-α-cyano-3-phenoxybenzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxybenzyl(Z)-(1S)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin.

Cyhalothrin is a known compound and exist in 4 isomeric forms namely :

the ester derived from (+) cis acid and α-(S)-alcohol (isomer 1),

the ester derived from (-) cis acid and α-(R)-alcohol (isomer 2)

the ester derived from (+) cis acid and α-(R)-alcohol (isomer 3) and

the ester derived from (-) cis and α-(S)- alcohol (isomer 4).

Isomers 1 and 2 form one enantiomeric pair, whereas isomers 3 and 4 form another enantiomeric pair.

It has been scientifically established that isomer 1 is only insecticidally active, whereas the other isomers are practically inactive. Preparation of isomer 1 by stereoselective synthesis and resolution is possible but these routes are very expensive and economically not viable. Isomer 1 is, however, always acompanied by isomer 2 due to identical physical properties of both. Therefore, the enantiomeric pair of isomers 1 and 2 has been commercially

used as the insecticidally active component of cyhalothrin and this enantiomeric pair is known as lamba cyhalothrin.

European Patent No EP 10 72 96 discloses a process for preparation of lambda cyhalothrin by epimerisation-crystallisation of cyhalothrin in an organic solvent in the presence of a base with pure crystals of said enantiomeric mixture as seeding agent at 10 to -20°C. The process results in low yield of the order of about 70% and takes about 32 hours. The process thus takes long duration and results in low yield besides requiring considerable amount of energy. It is, therefore, difficult and inconvenient to carry out and uneconomical.

It has been found out by us by extensive research and experimentation that the rate of epimerisation crystallisation of cyhalothrin is increased by carrying it out in an alcohol catalysed by 1,4-diazabicyclo (2,2,2) octane (DABCO).

Accordingly the object of the invention is to provide a process for the preparation of the insecticidal enantiomeric mixture of (S)- α-cyano-3-phenoxybenzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl-cyclopropane carboxylate and (R)- α -cyano-3-phenoxybenzyl-(Z)-(1S)-cis-3-(2-chloro-3,3,3-trifluoro propenyl)-2,2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin which is of short duration and requires less energy and is easy and convenient to carry out and is economical and gives the product in high yield and purity.

According to the invention there is provided a process for the preparation of the insecticidal enantiomeric mixture of (S)-α -cyano-3-phenoxy benzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl cyclopropane carboxylate and (R)-α -cyano-3-phenoxybenzyl-(Z)-(1S)-cis-3(2-chloro-3,3,3-trifluoro propenyl)-2,2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin by epimerisation crystallisation of cyhalothrin in an alcohol in the presence of 1,4-diazabicyclo(2,2,2) octane (DABCO) with pure crystals of said enantiomeric mixture as seeding agent at 20°C to 0°C.

The alcohol is for example, methanol, ethanol or isopropyl alcohol preferably methanol.

The process of the invention is of short duration of the order of 10 hours. The reason for the short duration of the process is possibly because of the strong basic nature and steric hindrance of DABCO which favours enhanced epimerisation. Because of the short duration there is saving in energy and time making the process easy and convenient to carryout, cost effective and cheap. The process also gives the product in high yield and purity.

The following example is illustrative of the invention but not limitative of the scope thereof.

Example 1

A mixture of 200 parts of cyhalothrin containing 42% by weight of the isomers 1 and 2 and 58% by weight of the isomers 3 and 4 was taken in 160 parts of methanol and 0.5 parts of DABCO was added to it and stirred at 15-20° for 4 hrs. The reaction was cooled to 0°C. 4.0 parts of pure crystals of the enatiomeric pair of isomers 1 and 2 was added to it and maintained at 0°C for 6 hrs. The solids were filtered, washed with chilled methanol and dried in a desicator containing P_2O_5. Yield : 160 gm. 80%. Purity : 94%.

We Claim :

178538

1. A process for the preparation of the insecticidal enantiomeric mixture of (S)-α-cyano-3-phenoxy benzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxy-benzyl-(Z)-(1S)-cis-3(2-chloro-3,3,3-trifluoro propenyl)-2,2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin by epimerisation crystallisation of cyhalothrin in an alcohol in the presence of 1,4-diazabicyclo (2,2,2) octane (DABCO) with pure crystals of said enantiomeric mixture as seeding agent at 20° to 0°C.

2. A process as claimed in claim 1, wherein the alcohol is methanol.

3. A process for the preparation of the insecticidal enantiomeric mixture of (S)-α-cyano-3-phenoxy benzyl-(Z)-(1R)-cis-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethyl cyclopropane carboxylate and (R)-α-cyano-3-phenoxy-benzyl-(Z)-(1S)-cis-3(2-chloro-3,3,3-trifluoro propenyl)-2,2-dimethyl cyclopropane carboxylate, commonly known as lambda cyhalothrin substantially as herein described particularly with reference to the example 1.

Dated this 25th day of May 1995.

(H A Jose)
of DePENNING & DePENNING
Agent for the Applicants